

Second order phase transitions and thermodynamic geometry: a general approach

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Abstract.

In this work we relate the curvature of distinct thermodynamic geometries to the response functions of any thermodynamic system with two degrees of freedom. In this manner it is straightforward to identify which geometry describes more accurately second order phase transitions. According to our results, Quevedo's metric g^{II} in general behaves better than Weinhold and Ruppeiner's, although in principle ambiguities might appear. It is possible to analyze the problem of describing second order phase transitions through the scalar curvature from a different perspective. For this, we propose a general criterion starting from a particular form of the curvature scalar.

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1. Introduction

Ever since Weinhold [1, 2] proposed in the seventies to use Riemannian geometry to study thermodynamic systems, there has been a significant number of papers studying the physical properties of systems by means of this formalism. This is done using the curvature of the Riemannian manifold representing the equilibrium space of thermodynamics, associating divergences of the curvature to phase transitions. Furthermore, Ruppeiner [3] proposed a different metric structure for the equilibrium space, developed from considerations about thermodynamic fluctuation theory. Weinhold's metric components are those of the Hessian of the internal energy function of the system, while Ruppeiner's are defined in terms of the Hessian of the entropy fundamental relation. It turns out that Ruppeiner's metric is conformally related to Weinhold's [4]. Recently, Quevedo [5] suggested to make use of Legendre invariant metrics in order to get a geometric description of thermodynamics which does not depend on the election of the thermodynamic potential, this approach is known as Geometrothermodynamics (GTD).

Besides these thermodynamic geometries, an important and related approach in this context is Fisher-Rao geometry [6, 7], also called information geometry, which starts from statistical mechanics distributions to build the metric. A good and recent review on this topic is the work of Brody [7], in which there is also an extensive bibliographical note and the relation between Fisher-Rao geometry and Ruppeiner's (hence Weinhold's) geometry is presented. We will not deal with Fisher-Rao's information geometry in this work, focusing our attention on the metrics arising from thermodynamics only.

We will not describe in detail these geometries in this paper, referring the interested reader to the bibliography, for instance see [5, 8] and references therein. We would like to mention only two facts about these geometric approaches:

1. Some encouraging results have been found from testing these geometries on physical systems [1, 9, 8, 10], as long as some puzzling situations [11, 12, 13]. In particular, a lot of work has been devoted to the study of black holes thermodynamic geometry [14, 15, 16, 17, 18, 19, 20].
2. So far, every work based on the above geometric approaches has followed the same path, analyzing a particular system at a time. Namely, first a physical system and a metric are chosen and the curvature is computed, then the thermodynamic quantities (e.g. heat capacities) are evaluated and finally the results are compared.

Indeed, after almost 40 years of work in this direction, still there is no agreement on which metric should be used for thermodynamic geometry to reproduce the physical properties of any system. Even more, it is not clear yet how such a metric should be constructed.

In this paper we want to address the question of how to compare thermodynamic geometries from a general and thermodynamical point of view. In particular, what we will do is to obtain the curvature of all these geometries in terms of the thermodynamic

quantities that describe second order phase transitions. This is usually the case of black holes [21]. As simple as it seems, with our criterion one immediately can distinguish which is the best metric for reproducing second order phase transitions within the set of the existing ones. As a result of our work, Weinhold and Ruppeiner's metrics seem to be less accurate than Quevedo's metric g^{II} (see [8]), as we will see in sections 2 and 3. However, from the form of the curvature of g^{II} in terms of the response functions, some divergences might appear which are not related to phase transitions, although up to now no physical example of this situation has been found. To avoid this kind of problems, we suggest what should be the form of the curvature (see eq. (23)) and present a new family of metrics (eq. (22)) that describe unambiguously second order phase transitions as curvature singularities.

The paper is organized as follows. In section 2 we will introduce Ruppeiner and Weinhold's metrics and evaluate their curvature in terms of physical quantities. In section 3 we will analyze Quevedo's metric g^{II} and find the physical expression for its curvature. In section 4 an ad hoc thermodynamic family of metrics for second order phase transitions is discussed. Finally, in section 5 we will analyze the results and discuss further perspectives.

2. Ruppeiner and Weinhold's geometries.

Weinhold's metric is defined [1, 2] as the Hessian of the free energy U , i.e. in two dimensions it is the metric

$$g^W = \frac{\partial^2 U}{\partial S^2} dS^2 + 2 \frac{\partial^2 U}{\partial S \partial V} dS dV + \frac{\partial^2 U}{\partial V^2} dV^2. \quad (1)$$

First we observe that one can rewrite this metric in a more physical fashion using the heat capacity at constant volume, the isentropic compressibility and the isentropic thermal expansion (sometimes the isentropic compressibility is referred to as adiabatic compressibility which it is only correct for reversible processes). In fact, the heat capacity and the compressibility are defined as [22, 23]

$$C_V = \frac{\partial U}{\partial S} \left(\frac{\partial^2 U}{\partial S^2} \right)^{-1} = T \left(\frac{\partial^2 U}{\partial S^2} \right)_V^{-1}, \quad (2)$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = \frac{1}{V} \left(\frac{\partial^2 U}{\partial V^2} \right)_S^{-1}, \quad (3)$$

whereas the isentropic thermal expansion is

$$\alpha_S = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_S = \frac{1}{V} \left(\frac{\partial^2 U}{\partial V \partial S} \right)_S^{-1}. \quad (4)$$

Hence Weinhold's metric can be rewritten as

$$g^W = \frac{T}{C_V} dS^2 + \frac{2}{V \alpha_S} dS dV + \frac{1}{V \kappa_S} dV^2. \quad (5)$$

Starting from this metric, one can compute the curvature as a function of the physical quantities C_V , κ_S and α_S , the result being

$$R^W = \frac{1}{\mathcal{P}(C_V, \kappa_S, \alpha_S)} \left\{ \begin{aligned} & \left[(A_1 + A_2 \alpha_S) \kappa_S^4 + (A_3 \alpha_S^2 + A_4 \alpha_S^3) \kappa_S^2 + A_5 \alpha_S^3 \kappa_S \right] C_V^4 \\ & + \left[(A_6 \alpha_S^2 + A_7 \alpha_S^3) \kappa_S^3 + A_8 \alpha_S^3 \kappa_S^2 + A_9 \alpha_S^5 \kappa_S + A_{10} \alpha_S^5 \right] C_V^3 \\ & + \left[(A_{11} \alpha_S^2 + A_{12} \alpha_S^3) \kappa_S^4 + (A_{13} \alpha_S^3 + A_{14} \alpha_S^4) \kappa_S^3 + A_{15} \alpha_S^4 \kappa_S^2 + A_{16} \alpha_S^5 \kappa_S \right] C_V^2 \\ & + \left[A_{17} \alpha_S^3 \kappa_S^4 + (A_{18} \alpha_S^4 + A_{19} \alpha_S^5) \kappa_S^3 + A_{20} \alpha_S^5 \kappa_S^2 \right] C_V + A_{21} \alpha_S^5 \kappa_S^3 \end{aligned} \right\}, \quad (6)$$

where

$$\mathcal{P}(C_V, \kappa_S, \alpha_S) = C_V^2 \kappa_S^2 \alpha_S [TV \alpha_S^2 - C_V \kappa_S]^2 \quad (7)$$

and A_i for $i = 1, \dots, 21$ are functions of the variables T, V and of the derivatives up to second order of C_V , κ_S and α_S with respect to S and V (in particular, the A_i 's do not depend on C_V and κ_S).

Usually for thermodynamic systems, second order phase transitions are signaled by the divergences of C_V and κ_S (see e.g. for ordinary systems [22] and for black holes [21]). Expression (6) is important because it directly relates the scalar curvature of Weinhold's metric to these quantities. If thermodynamic geometry wishes to reproduce phase transitions using the curvature, divergences of the curvature should coincide with divergences of the heat capacity and isentropic compressibility. Let us analyze what is the behaviour of the thermodynamic curvature as C_V and κ_S tend to infinity. From eqs. (6) and (7), we immediately notice that

$$\lim_{C_V \rightarrow \infty} R^W = \frac{(A_1 + A_2 \alpha_S) \kappa_S^4 + (A_3 \alpha_S^2 + A_4 \alpha_S^3) \kappa_S^2 + A_5 \alpha_S^3 \kappa_S}{\alpha_S \kappa_S^4} \Big|_{T_c, V_c} \quad (8)$$

and

$$\lim_{\kappa_S \rightarrow \infty} R^W = \frac{(A_1 + A_2 \alpha_S) C_V^4 + (A_{11} \alpha_S^2 + A_{12} \alpha_S^3) C_V^2 + A_{17} \alpha_S^3 C_V}{\alpha_S C_V^4} \Big|_{T_c, V_c}, \quad (9)$$

where T_c and V_c stand for the critical values of the thermodynamic variables at the phase transition point. *In most of the cases* the limits in eqs. (8) and (9) are finite and show that Weinhold's geometry cannot in general reproduce the singularities in the heat capacity, hence under this criterion it is not a satisfactory choice, since it may yield to misleading results when seeking second order phase transitions. The Reissner-Nördstrom black hole provides an example of such a failure, since Weinhold's geometry is flat, contrary to the appearance of a singularity in the heat capacity [11]. Nevertheless, it might happen that for some particular systems the curvature diverges at the critical point, but this is rather a coincidence than a general fact.

The limit of the curvature when the isentropic thermal expansion α_S tends to infinity is of the same form as in eqs. (8) and (9), although it is not clear if the divergence of α_S is related to second order phase transitions. [23]

Let us now analyze Ruppeiner's metric. This metric is defined [3] as the Hessian of the entropy. Thus it is written in its natural variables as

$$g^R = -\left(\frac{\partial^2 S}{\partial U^2} dU^2 + 2 \frac{\partial^2 S}{\partial U \partial V} dU dV + \frac{\partial^2 S}{\partial V^2} dV^2\right). \quad (10)$$

In principle one cannot write this metric in terms of C_V , κ_S and α_S , because they are derivatives of U and not of S . Nevertheless, we observe that there is a relation between Ruppeiner and Weinhold's geometries [4], that is

$$g^R = \frac{1}{T} g^W. \quad (11)$$

Eqs. (5) and (11) allow us to rewrite Ruppeiner's geometry as

$$g^R = \frac{1}{T} \left(\frac{T}{C_V} dS^2 + \frac{2}{V\alpha_S} dS dV + \frac{1}{\kappa_S V} dV^2 \right). \quad (12)$$

In Appendix A we present the curvature and its corresponding limits. There we argue that, as in the case of Weinhold, Ruppeiner's curvature scalar in general tends to finite expressions when C_V or κ_S tend to infinity (the same for α_S). Indeed, we can conclude as for Weinhold's geometry, that Ruppeiner's geometry is not precise to describe second order phase transitions. To conclude this section, we want to point out that our results are obtained *in general* and we evaluate the limits for some diverging quantity keeping all the thermodynamic variables finite. This means that it might happen that Weinhold and Ruppeiner's metrics can actually reproduce second order phase transitions for particular thermodynamic systems, although this is not true in general [24]. In the next section we present a metric whose curvature diverges at those points where C_V and κ_S do, making it a better candidate for a geometric description of second order phase transitions.

3. Quevedo's geometries.

Quevedo [5] has proposed a new approach in the context of thermodynamic geometry coined as Geometrothermodynamics (GTD). In this program metrics are derived imposing Legendre invariance, in order to reproduce the invariance properties of ordinary thermodynamics[5]. These metrics have proven to be appropriate to describe the thermodynamics of different systems. In particular, it is argued [8] that there is a metric which seems to accurately reproduce the thermodynamics of black holes or, more in general, of systems with second order phase transitions. Its expression in general coordinates, following the notation of [8], is

$$g^{II} = \left(E^c \frac{\partial \Phi}{\partial E^c} \right) \left(\eta_{ab} \delta^{bf} \frac{\partial^2 \Phi}{\partial E^f \partial E^d} dE^a dE^d \right), \quad (13)$$

where the superscript II indicates that it is a metric that reproduces second order transitions, Φ is the thermodynamic potential, E^a are the extensive variables of this potential, and Einstein summation convention is used. In [13] it is investigated in detail the problem of invariance in Geometrothermodynamics and it is pointed out

that, although this metric is invariant under total Legendre transformations, the same situation does not hold for a change of representation, so that the geometry is different if one chooses the energy U or the entropy S in (13) as the thermodynamic potential. For this reason, we now write its expression in the U representation, which reads

$$g_U^{II} = (S \partial_S U + V \partial_V U)(-\partial_S^2 U dS^2 + \partial_V^2 U dV^2), \quad (14)$$

where $\partial_X U \equiv \frac{\partial U}{\partial X}$. Using the definitions (2), (3) and the conditions of equilibrium $\partial_S U = T$, $\partial_V U = -P$, we can rewrite this metric in terms of the physical quantities, obtaining

$$g_U^{II} = (TS - PV) \left(-\frac{T}{C_V} dS^2 + \frac{1}{V\kappa_S} dV^2 \right). \quad (15)$$

From eq. (15) we can compute the curvature of g_U^{II} in terms of C_V , κ_S and α_S , obtaining

$$\begin{aligned} R_U^{II} = & \left[(B_1 + B_2\alpha_S^{-1} + B_3\alpha_S^{-2}) + (B_4 + B_5\alpha_S^{-1})\kappa_S^{-1} + B_6\kappa_S^{-2} \right] C_V \\ & + \left[(B_7 + B_8\alpha_S^{-1} + B_9\alpha_S^{-2})\kappa_S + (B_{10} + B_{11}\alpha_S^{-1}) + B_{13}\kappa_S^{-1} \right] \\ & + \left[(B_{14} + B_{15}\alpha_S^{-1})\kappa_S + B_{16} \right] C_V^{-1} + B_{17}\kappa_S C_V^{-2}, \end{aligned} \quad (16)$$

where B_i for $i = 1, \dots, 17$ are functions of the variables T, V, P, S and of the derivatives up to second order of C_V , κ_S and α_S with respect to S and V (in particular, the B_i 's do not depend on C_V and κ_S).

Assuming that the factors accompanying each of the different powers of C_V are non vanishing and finite at the critical points, we immediately see that

$$\lim_{C_V \rightarrow \infty} R_U^{II} = \pm\infty, \quad (17)$$

and the same can be said about the limit when κ_S tends to infinity,

$$\lim_{\kappa_S \rightarrow \infty} R_U^{II} = \pm\infty. \quad (18)$$

The last two equations clearly indicate that at those points where a second order phase transition occurs the curvature diverges. Therefore, this is the general behaviour of the curvature at the critical points. It is important to consider the possibility that for a particular system the functions B_i might be such that the limits (17) and (18) are no longer true. However, we stress the fact that up to now every physical system that has been studied using g^{II} is in accordance with the limits (17) and (18) [8, 12, 24].

Furthermore, the curvature diverges also at those points where C_V , κ_S and α_S change sign, which is also a desirable property, for these points are usually associated with a change in the stability of the system [21].

Let us now explore the case where the potential used in eq. (13) is S , i.e. the entropy representation. As we have already pointed out, the geometry will be different in general from the geometry of g_U^{II} , so we have to study it separately. In this representation, metric (13) reads

$$g_S^{II} = (U \partial_U S + V \partial_V S)(-\partial_U^2 S dU^2 + \partial_V^2 S dV^2). \quad (19)$$

As in the case of Ruppeiner's metric (eq. (10)), we need an expression for this metric in terms of the derivatives of U in order to make C_V and κ_S appear in it. However, there is a relation between g_S^{II} and g_U^{II} (analogous to eq. (11) for Ruppeiner and Weinhold's metrics), this relation being [13]

$$g_S^{II} = -\frac{U + PV}{(TS - PV)T^2} g_U^{II}. \quad (20)$$

From eqs. (15) and (20), g_S^{II} in terms of the physical quantities reads

$$g_S^{II} = -\frac{U + PV}{T^2} \left(-\frac{T}{C_V} dS^2 + \frac{1}{V\kappa_S} dV^2 \right). \quad (21)$$

With this expression we evaluate the curvature and find out a result completely similar to eq. (16). In particular, the divergences of the heat capacity and those of the compressibility and their change of sign are reproduced as curvature singularities. Thus we conclude that g^{II} is well behaved in both representations.

For the sake of completeness, we comment that we have also examined other metrics which are present in the context of Geometrothermodynamics which seem to be appropriate to describe first order transitions [8]. For these metrics we obtained results for second order phase transitions which are never as good as the ones just obtained with g^{II} , hence we will not discuss them. We conclude that, among the existing and already studied thermodynamic geometries, Quevedo's metric g^{II} appears to be the best one to reproduce second order phase transitions.

To end this section, we remark that our results are obtained *in general* and we evaluate the limits for some diverging quantity keeping all the thermodynamic variables finite. This means that, due to the fact that in (16) the coefficients are not constant, there could be in principle some very unfortunate cases when Quevedo's g^{II} metric can happen to not reproduce second order phase transitions, that would be the case if the coefficient of C_V in (16) vanishes at the point where C_V diverges. For the same reason, it might occur that the curvature has some additional singularities which do not appear in the response functions. This means that this metric, though being the most accurate among the ones already existing in the literature, it is in principle not free of ambiguities. In the next section we will present a condition a metric should satisfy to be guaranteed that it will always reproduce the second order transitions structure.

4. Curvature and second order phase transitions

In this section we present a family of thermodynamic metrics which exactly reproduce, as singularities in the curvature, the second order phase transitions described by divergences of the response functions. These metrics are written in terms of C_V and κ_S as,

$$ds^2 = \exp[-(aC_V^2 + b\kappa_S^2)] (A dS^2 + B dV^2), \quad (22)$$

where a and b are appropriate positive constants and A and B are arbitrary non vanishing constants. The curvature for these metrics reads

$$R = \frac{2 \exp[aC_V^2 + b\kappa_S^2]}{AB} \left\{ a[B(\partial_S C_V)^2 + BC_V \partial_S^2 C_V + A(\partial_V C_V)^2 + AC_V \partial_V^2 C_V] \right. \\ \left. + b[B(\partial_S \kappa_S)^2 + B\kappa_S \partial_S^2 \kappa_S + A(\partial_V \kappa_S)^2 + A\kappa_S \partial_V^2 \kappa_S] \right\}. \quad (23)$$

Notice that the above expression has two factors which both diverge when C_V and κ_S tend to infinity (the first factor clearly diverges when C_V and κ_S do and the second factor also does, since we are dealing with vertical asymptotes of these quantities). Therefore, it is clear that this curvature fulfills

$$\lim_{C_V \rightarrow \infty} R(C_V, \kappa_S) = \pm\infty \quad \text{and} \quad \lim_{\kappa_S \rightarrow \infty} R(C_V, \kappa_S) = \pm\infty. \quad (24)$$

Another choice to obtain (24) is that the curvature is expressed as a linear combination (with positive coefficients) of the square of the heat capacity and the square of the isentropic compressibility, that is,

$$R = a_1 C_V^2 + a_2 \kappa_S^2, \quad a_1, a_2 \in \mathbb{R}^+. \quad (25)$$

One can go further and ask that the curvature reproduce also the change of signs in C_V and κ_S . Then the equation for the curvature reads

$$R = a_1 C_V^2 + a_2 \kappa_S^2 + a_3 \frac{1}{C_V^2} + a_4 \frac{1}{\kappa_S^2}, \quad a_1, a_2, a_3, a_4 \in \mathbb{R}^+. \quad (26)$$

It is worth to mention again that the sole purpose of the metrics (22) is to describe second order phase transitions by divergences of the curvature scalar and in principle not to assign a further meaning to the curvature. For instance, these metrics are not Legendre invariant as it is Quevedo's g^{II} . It would be interesting to find out if these metrics have any physical origin.

5. Conclusions and Perspectives

In this work we calculated the general expressions for the curvature scalars of Weinhold, Ruppeiner and Quevedo's geometries in terms of the response functions. The limits when each of the response functions tends to infinity were taken for these curvatures. From these limits we explain in a simple and general manner why a phase transition described by a divergence in a response function can be identified with a curvature singularity.

For Weinhold and Ruppeiner's curvatures it turns out that the scalars in general remain finite, which means that they cannot properly describe second order transitions. On the contrary, Quevedo's curvature diverges at those limits, thus indicating that it is a better candidate to describe second order phase transitions.

Moreover, we found a family of metrics (22) whose curvature (23) readily fulfills the task of diverging if and only if the response functions diverge. With the use of these metrics, it is possible to describe unambiguously second order phase transitions as curvature singularities.

We would like to stress that we are only focusing on the behaviour of thermodynamic geometries with respect to second order phase transitions points, leaving aside any other physical or invariance property of the metric.

We believe that this work could be the starting point to a more detailed and wider analysis of phase transitions from the geometric point of view, that eventually will lead us to a geometric definition of phase transitions.

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Appendix A. Curvature expressions and limits

The curvature of Ruppeiner's metric (12) is

$$\begin{aligned}
 R^R = \frac{-1}{\mathcal{P}(C_V, \kappa_S, \alpha_S)} & \left\{ \left[(A_1 + A_2 \alpha_S) \kappa_S^4 + (A_3 \alpha_S^2 + A_4 \alpha_S^3) \kappa_S^2 + A_5 \alpha_S^3 \kappa_S \right] C_V^4 \right. \\
 & + \left[(A_6 \alpha_S^2 + A_7 \alpha_S^3) \kappa_S^3 + A_8 \alpha_S^3 \kappa_S^2 + A_9 \alpha_S^5 \kappa_S + A_{10} \alpha_S^5 \right] C_V^3 \\
 & + \left[(A_{11} \alpha_S^2 + A_{12} \alpha_S^3) \kappa_S^4 + (A_{13} \alpha_S^3 + A_{14} \alpha_S^4) \kappa_S^3 \right. \\
 & \quad \left. + (A_{15} \alpha_S^4 + A_{16} \alpha_S^5) \kappa_S^2 + A_{17} \alpha_S^5 \kappa_S \right] C_V^2 \\
 & \left. + \left[A_{18} \alpha_S^3 \kappa_S^4 + (A_{19} \alpha_S^4 + A_{20} \alpha_S^5) \kappa_S^3 + A_{21} \alpha_S^5 \kappa_S^2 \right] C_V + A_{22} \alpha_S^5 \kappa_S^3 \right\}, \quad (\text{A.1})
 \end{aligned}$$

where

$$\mathcal{P}(C_V, \kappa_S, \alpha_S) = C_V^2 \kappa_S^2 \alpha_S [TV \alpha_S^2 - C_V \kappa_S]^2 \quad (\text{A.2})$$

and A_i for $i = 1, \dots, 22$ are functions of the variables T, V and of the derivatives up to second order of C_V, κ_S and α_S with respect to S and V (in particular, the A_i s do not depend on C_V and κ_S). Notice that here the functions A_i are different from the ones in (6). The limits when C_V and κ_S tend to infinity are of the same form as for eqs. (8) and (9). Therefore, Ruppeiner's approach suffers the same inaccuracy as Weinhold's.

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